# Sertifikaat

REPUBLIEK VAN SUID AFRIKA

PATENT KANTOOR DEPARTEMENT VAN HANDEL **EN NYWERHEID** 



Certificate

REPUBLIC OF SOUTH AFRICA

PATENT OFFICE DEPARTMENT OF TRADE AND **INDUSTRY** 

Hiermee word gesertifiseer dat This is to certify that

the documents annexed hereto are true copies of:

PCT Application No. PCT/ZA02/00024 filed with the South African Receiving Office on 06 March 2002 in the name of BILLITON SA LIMITED for an invention entitled: "RECOVERY OF METALS FROM JAROSITE-CONTAINING MATERIALS"

eteken te

**PRETORIA** 

in die Republiek van Suid-Afrika, hierdie

in the Republic of South Africa, this

March 2005

Registrar of Patents



#### Original (for SUBMISSION) - printed on 05.03.2002 09:05:53 AM

0	For receiving Office was anti-			
	For receiving Office use only	BCT /7800100000		
0-1	International Application No.	PCT/ZA02/00024		
0-2	International Filing Date	0 6 MAR 2002		
0-3	Name of receiving Office and "PCT International Application"	SAPTO		
	T			
0-4	Form - PCT/RO/101 PCT Request			
0-4-1	Prepared using	PCT-EASY Version 2.92		
	·	(updated 01.03.2001)		
0-5	Petition			
	The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty			
0-6	Receiving Office (specified by the applicant)	South African Patents and Trade Marks Office (RO/ZA)		
0-7	Applicant's or agent's file reference	INT1046/MAJR		
1	Title of invention	RECOVERY OF METALS FROM		
		JAROSITE-CONTAINING MATERIALS		
11	Applicant			
II-1	This person is:	applicant only		
II-2	Applicant for	all designated States except US		
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		South Africa		
III-1-6	State of nationality	ZA		
111-1-7	State of residence	ZA		

REGISTRAR OF PATENTS DESIGNS, TRADE MARKS AND COPYRIGHT

2002 -03- 06

REGISTRATEUR VAN PATENTE, MODELLE, HANDELSMERKE EN OUTEURSREG

#### **PCT REQUEST**

# INT1046/MAJR Original (for SUBMISSION) - printed on 05.03;2002 09:05:53 AM

111-2	Applicant and/or inventor	
III-2-1	This person is:	applicant and inventor
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111-2-4	Name (LAST, First)	SCHAEKERS, Jozef, Marie
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111-2-7	State of residence	ZA
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# PCT REQUEST

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V	Designation of States			
V V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AP: GH GM KE LS MW MZ SD SL SZ TZ UG ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE TR and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GQ GW ML MR		
		NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT		
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH&LI CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PH PL PT RO RU SD SE SG SI SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW		
V-5	Precautionary Designation Statement	12 04 00 00 02 44 10 24 24		
	In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.			
V-6	Exclusion(s) from precautionary designations	NONE		
VI-1	Priority claim of earlier national application	·		
VI-1-1	Filing date	08 March 2001 (08.03.2001)		
VI-1-2	Number	2001/1927		
VI-1-3	Country	ZA		
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)		

# PCT REQUEST

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VIII	Declarations	Number of declarations			
VIII-1	Declaration as to the identity of the	-			
	inventor	•			
VIII-2	Declaration as to the applicant's entitlement, as at the international filing	<del>'</del> –			
	date, to apply for and be granted a patent		İ		
VIII-3	Declaration as to the applicant's	_			
	entitlement, as at the international filing		1		
	date, to claim the priority of the earlier application	,			
VIII-4	Declaration of inventorship (only for the				
VIII	purposes of the designation of the United				
	States of America)				
VIII-5	Declaration as to non-prejudicial	_			
	disclosures or exceptions to lack of novelty				
īX	Check list	number of sheets	electronic file(s) attached		
IX-1	Request (including declaration sheets)	5	_		
IX-2	Description	11			
IX-3	Claims	3			
IX-4	Abstract	1	EZABSTOO.TXT		
IX-5	Drawings	1	_		
IX-7	TOTAL	21			
	Accompanying items	paper document(s) attached	electronic file(s) attached		
IX-8	Fee calculation sheet	<b>√</b>	-		
IX-10	Original general power of attorney	<b>√</b>	-		
IX-10	Original general power of attorney	<b>√</b>	-		
IX-10	Original general power of attorney	✓	-		
IX-17	PCT-EASY diskette	-	Diskette		
IX-19	Figure of the drawings which should	1			
IX-20	accompany the abstract				
IX-20	Language of filing of the international application	English			
X-1	Signature of applicant, agent or	1111			
	common representative				
		100011	-		
X-1-1	Name	MCCALLUM RADEMEYER &	FREIMOND		
X-1-2	Name of signatory	MAJ Rademeyer			
X-1-3	Capacity	Agent			
	, ,	Adent			

#### FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	0 6 MAR 2002	
10-2	Drawings:		
10-2-1	Received		
10-2-2	Not received		
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application		

INT1046/MAJR

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#### **PCT REQUEST**

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Original (for SUBMISSION)	<ul> <li>printed on 05.03.2002</li> </ul>	09:05:53 AM
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10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/EP '
10-6	Transmittal of search copy delayed until search fee is paid	

# FOR INTERNATIONAL BUREAU USE ONLY

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44 4	Data of reasing of the research convention	
11-1	Date of receipt of the record copy by	
	I the International Bureau	
	i tile international bureau	
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Printed on 22.01.2002 08:46:50 AM

#### **PCT POWER OF ATTORNEY**

INT1046/MAJR

0-1	PCT Power of Attorney (for an international application filed under the Patent Cooperation Treaty) (PCT Rule 90.4)		
0-1-1	Prepared using	PCT-EASY Version 2.92 (updated 01.03.2001)	
1	The undersigned applicant(s)	SCHAEKERS, Jozef, Marie	
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1-2	as	agent	
1-3	to represent the undersigned before	all the competent International Authorities	
1-4	in connection with the international application identified below:		
1-4-1	Title of the invention	RECOVERY OF METALS FROM JAROSITE-CONTAINING MATERIALS	
1-4-2	Applicant's or agent's file reference	INT1046/MAJR	
1-4-3	International application number (if already available)		
1-4-4	filed with the following Office as receiving Office	South African Patents and Trade Marks Office (RO/ZA)	
1-5	and to make or receive payments on behalf of the undersigned.		
2-3	Signature of applicant	A	
2-3-1	Name	SCHAEKERS, Jozef, Marie	
3	Date	22 January 2002 (22.01.2002)	

#### PCT POWER OF ATTORNEY

INT1046/MAJR

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0-1	PCT Power of Attorney (for an international application filed under the Patent Cooperation Treaty) (PCT Rule 90.4)	
0-1-1	Prepared using	PCT-EASY Version 2.92
		(updated 01.03.2001)
1	The undersigned applicant(s)	AHERN, Noelene
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1-3	to represent the undersigned before	all the competent International
		Authorities
1-4	in connection with the international application identified below:	
1-4-1	Title of the invention	RECOVERY OF METALS FROM
		JAROSITE-CONTAINING MATERIALS
1-4-2	Applicant's or agent's file reference	INT1046/MAJR
1-4-3	International application number (if already available)	
1-4-4	filed with the following Office as	South African Patents and Trade Marks
	receiving Office	Office (RO/ZA)
1-5	and to make or receive payments on behalf of the undersigned.	
	<u> </u>	
2-2	Signature of applicant	* Mhen ~
2-2-1	Name	AHERN, Noelene
3	Date	22 January 2002 (22.01.2002)

#### PCT POWER OF ATTORNEY

#### INT1046/MAJR

#### Printed on 22.01.2002 08:46:35 AM

0-1	PCT Power of Attorney (for an international application filed under the Patent Cooperation Treaty) (PCT Rule 90.4)	•		
0-1-1	Prepared using .	PCT-EASY Version 2.92		
		(updated 01.03.2001)		
1	The made is a decision of the second			
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1-2	as	agent		
1-3	to represent the undersigned before	all the competent International		
		Authorities		
1-4	in connection with the international			
1-4-1	application identified below: Title of the invention	DECOMENY OF VERNIC EDOM		
1-4-1	The of the invention	RECOVERY OF METALS FROM		
1-4-2	Applicant's or agent's file	JAROSITE-CONTAINING MATERIALS		
1-4-2	reference	INT1046/MAJR		
1-4-3	International application number (if already available)			
1-4-4	filed with the following Office as	South African Patents and Trade Marks		
	receiving Office	Office (RO/ZA)		
1-5	and to make or receive payments on behalf of the undersigned.			
2-1	Signature of applicant	Marie III		
		P.M. CRAVEN		
	<u> </u>	VICE PRESIDENT - TECHNOLOGY		
2-1-1	Name	BILLITON SA LIMITED		
3	Date	22 January 2002 (22.01.2002)		

# PCT (ANNEX - FEE CALCULATION SHEET) Original (for SUBMISSION) - printed on 05.03.2002 09:05:53 AM

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(This sheet is not part of and does not count as a sheet of the international application)

0	For receiving Office use only	, .		
0-1	International Application No.			
0-2	Date stamp of the receiving Office	0.6 M	AR 2002	
0-4	Form - PCT/RO/101 (Annex) PCT Fee Calculation Sheet			
0-4-1	Prepared using	PCT-EASY Vers	ion 2.92	
		(updated 01.0	3.2001)	
0-9	Applicant's or agent's file reference	INT1046/MAJR		
2	Applicant	BILLITON SA L	IMITED, et al.	
12	Calculation of prescribed fees	fee amount/multiplier	total amounts (ZAR)	
12-1	Transmittal fee T	⇒	500	
12-2	Search fee S	₽	7,220	
12-3	International fee			
	Basic fee			
	(first 30 sheets) b1	3,152		
12-4	Remaining sheets	0		•
12-5	Additional amount (X)	72		
12-6	Total additional amount b2	0		
12-7	b1 + b2 = B	3,152		
12-8	Designation fees			
	Number of designations contained in international application	90		
12-9	Number of designation fees payable (maximum 6)	6		
12-10	Amount of designation fee (X)	680	]	
12-11	Total designation fees D	4,080		
12-12	PCT-EASY fee reduction R	-972	1	•
12-13	Total International fee (B+D-R)	⇨	6,260	***************************************
12-17	TOTAL FEES PAYABLE (T+S+I+P)	⇨	13,980	
12-19	Mode of payment	cheque	1	<u> </u>

#### **VALIDATION LOG AND REMARKS**

13-2-7	Validation messages Contents	Green?
İ		Priority 1. The priority document is not
		enclosed. (The applicant must furnish it
		within 16 months from the earliest
		priority date claimed)

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#### RECOVERY OF METALS FROM JAROSITE-CONTAINING MATERIALS

#### BACKGROUND OF THE INVENTION

This invention relates to the recovery of metals from jarosite-containing materials.

The leaching of certain metals. e.g. silver (Ag), lead (Pb) and zinc (Zn) using brine leaching, is well known. (1,2,3,4,5). The ease of solubilising these metals depends on the refractory nature of the material treated.

To improve recoveries from refractory materials by brine leaching, a combined high temperature oxidation process in combination with acidic brine leaching has been proposed. (4) A concentrate containing silver, mostly in sulfide minerals, yielded only 50 % Ag dissolution in a FeCl<sub>3</sub> brine leach. By leaching the concentrate at temperatures above 100°C with a high oxygen partial pressure in an acidic NaCl or CaCl<sub>2</sub> medium, the Ag recovery was increased to above 95 %.

Brine leaching alone is not effective in solubilising metals included in or encapsulated by jarosite or other similar iron hydroxy sulfate compounds since these compounds must first be decomposed.

Decomposition of jarosites in alkaline media is well known. Jarosites produced during pressure leaching of zinc concentrates were decomposed by treating the residues with a lime slurry at 90°C.<sup>(7)</sup> The following reactions were proposed to describe the reactions for hydronium jarosite, plumbojarosite and argentojarosite respectively:

 $H_3OFe_3(SO_4)_2(OH)_6 + 2Ca(OH)_2 + H_2O \rightarrow 3Fe(OH)_3 + 2CaSO_4.2H_2O$  $PbFe_6(SO_4)_4(OH)_{12} + 4Ca(OH)_2 + 8H_2O \rightarrow 6Fe(OH)_3 + Pb(OH)_2 + 4CaSO_4.2H_2O$  INT.1046/MAJR/jes

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 $AgFe_3(SO_4)_2(OH)_6 + 2Ca(OH)_2 + 4H_2O \rightarrow 3Fe(OH)_3 + AgOH + 2CaSO_4.2H_2O$ 

After liberation, Ag was subsequently recoverable by cyanidation. (7)

Destruction of jarosites produced in pressure leaching at 85°C to 90°C using an approximately stoichiometric quantity of lime, followed by cyanidation, improved Ag recoveries from less than 5 % to more than 97 %.<sup>(9)</sup>

NaOH has also been used to facilitate alkaline decomposition of jarosite-type materials before cyanidation. (8)

Leaching of jarosite-containing materials in an acidic brine medium of CaCl<sub>2</sub> at a temperature above the boiling point of the solution and elevated pressures, in the presence of lime or another suitable alkali to maintain the pH between 1.5 and 3.5, has been proposed to recover metals from jarosite. (6) Although this method was successful to recover Ag and Pb from jarosites the use of high pressures and temperatures is not always desirable.

It seems obvious that if metal recovery from jarosites is required, an alkaline pretreatment followed by cyanidation is a generally accepted and suitable method. However, cyanide has environmental disadvantages, and in some cases, cyanide consumption is too high for such a process to be economical, particularly in the presence of base metals like Cu, and sulfides.

Also, it is implied that jarosite-containing materials can be pretreated in an alkaline medium to liberate certain metals and that, once the metals are in suitable forms, brine leaching can be used to solubilise them. However, this treatment implies the use of a liquid/solid separation step between the alkaline decomposition stage and

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the acidic brine solubilisation, and additional process steps and costs. There would be advantages to eliminating this liquid/solid separation, by carrying out the alkaline decomposition in a brine medium followed immediately by acidification to solubilise the required metals. Also, the alkaline decomposition step is shown to be facilitated in a brine solution.

#### SUMMARY OF INVENTION

The invention provides a method to dissolve at least one metal from jarosite or other iron hydroxy sulfate-containing material which includes the steps of:

- a) subjecting the material to alkaline treatment in a brine solution to facilitate jarosite decomposition, and
- b) acidification of the brine slurry to solubilise the liberated metal.

The method may include the step of adjusting the pH of the brine slurry to remove solubilised iron or other impurities from the slurry followed by the step of separating metal-containing brine solution and solid residue from each other.

The metal value or values can be removed from the brine solution by any appropriate means selected, for example, from: cementation, ion exchange, solvent extraction, electrowinning and precipitation. After metal recovery, the barren brine liquor may be recycled to the alkaline treatment stage. A bleed stream may be introduced to control impurities, and additional NaCl and water may be added on recycle to compensate for any losses.

Preferably the temperature in the alkaline treatment stage is between 30°C and 100°C.

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Alkali may added to the brine solution in the form of lime, NaOH, LiOH or any other suitable alkali, or any combination thereof.

Preferably the brine concentration is between 100 g/l NaCl and saturation levels, or the equivalent of any other soluble chloride salt.

The temperature in the acidic brine leach stage may be between 30°C and 100°C.

The pH of the acidic brine leach stage is preferably less than 6.

The method may be used particularly for the recovery of silver.

#### BRIEF DESCRIPTION OF THE DRAWING

The invention is further described by way of examples with reference to the accompanying drawing which is a flow chart representation of the method of the invention.

#### DESCRIPTION OF PREFERRED EMBODIMENT

Referring to the accompanying drawing, a silver and jarosite-containing residue (10) is typically obtained by subjecting a silver-bearing material to a leaching process (e.g. bioleaching or pressure leaching) or by subjecting a silver and iron containing liquor to a precipitation process (e.g. iron removal).

The residue is subjected to an alkaline pretreatment in a brine medium (12). The liquid to solid ratio should be sufficient to ensure ease of operation and to ensure that no solubility constraints exist for the silver. The brine solution or slurry should contain from 100 g/l NaCl to saturation levels, preferably 200 g/l to 300 g/l. The

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brine solution may contain various impurities, including sulfate. Sulfate levels of up to 10 g/l may be acceptable, but less than 5 g/l are expected if lime is used as the alkali. The slurry should be maintained at a temperature of  $30^{\circ}$ C to  $100^{\circ}$ C, preferably  $50^{\circ}$ C  $- 90^{\circ}$ C.

An alkali (14), such as lime, is added to the slurry either to maintain an alkaline pH (>7), preferably greater than or equal to 9, and less than 13, or at a fixed addition rate based on the stoichiometry of the alkaline decomposition reaction.

The reaction is allowed to continue for a time depending on the composition of the material and the reaction temperature and pH. Usually a few hours are sufficient but more than 24 hours may be required in some cases, particularly in the lower pH or temperature ranges.

The alkaline brine slurry is then acidified (step 16), without any intermediate liquid/solid separation, by the addition of any suitable acid (18), preferably HCl or  $H_2SO_4$ , to a pH most suitable for the metal that is to be dissolved. For Ag, the pH should be greater than 0.1 and less than 6, preferably between 1 and 3.

The temperature of the acidic brine leach can be the same as that used in the alkaline pretreatment step (30°C – 100°C) and is preferably 70°C - 90°C.

As for the alkaline pretreatment stage, the residence time required for the acid leaching stage is variable, but is not expected to be longer than 8 hours.

An iron removal stage 20 may be included where the pH of the slurry is increased slightly by the addition of a suitable alkali 22, to precipitate iron. The pH should be less than 5.

After liquid/solid separation (24) to remove the solid residue 26, Ag is recovered by any suitable means, in this case, cementation 28 with Fe scrap 30. The Ag product is removed by liquid/solid separation (34) and the barren brine solution 36 is recycled to the alkaline pretreatment step (12).

Part of the brine solution 36 may be removed as a bleed stream 38 to control impurity build up. Also it may be necessary to add NaCl (40) and water 42 to make up the stream recycled to the stage 12.

#### Example 1

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A residue containing about 70% of Ag in jarosite was slurried with a 260 g/l NaCl solution at 80°C at a liquid to solid ratio of 10:1. The natural pH of the slurry ranged between 1.8 and 2.4. After leaching for 6 hours, the Ag dissolution was 22%.

This indicates that brine leaching alone is not sufficient to recover Ag from jarositetype materials.

#### Example 2

A residue containing about 70% of Ag in jarosite was slurried with a 260 g/l NaCl solution at 70 °C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to 145 kg Ca(OH)<sub>2</sub> per ton of sample, based on a stoichiometric excess of 20 %, and the slurry was agitated for 2 hours. The slurry was then acidified to pH 2 by adding 97 kg H<sub>2</sub>SO<sub>4</sub> per ton of sample, and agitated for a further 5 hours. Ag dissolution of 94 % was obtained.

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This illustrates the process of the invention using a fixed amount of alkali.

#### Example 3

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A residue containing about 70% of Ag in jarosite was slurried with a 260 g/l NaCl solution at 80°C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to maintain a constant pH of 9. After 3 hours, 126 kg Ca(OH)<sub>2</sub> per ton of sample had been consumed. The slurry was then acidified to pH 2 by adding 87 kg H<sub>2</sub>SO<sub>4</sub> per ton of sample and allowed to react for a further 5 hours. Ag dissolution of 93% was achieved.

This illustrates the process of the invention using a set pH during the alkali treatment.

#### Example 4

A residue containing about 70% of Ag in jarosite was slurried with a 260 g/l NaCl solution at 70°C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to maintain a constant pH of 9.5. After 4 hours, 181 kg Ca(OH)<sub>2</sub> per ton of sample had been consumed. The slurry was then acidified to pH 2 by adding 100 kg H<sub>2</sub>SO<sub>4</sub> per ton of sample and allowed to react for a further 5 hours. Ag dissolution of 94% was achieved.

This test was repeated, but excluding brine from the alkaline decomposition stage. After 24 hours, 83 kg Ca(OH)<sub>2</sub> per ton of sample had been consumed. The slurry was then acidified by adding 54 kg H<sub>2</sub>SO<sub>4</sub> per ton of sample and allowed to react for a further 5 hours. Ag dissolution of 43% was achieved.

This illustrates that the presence of brine in the alkaline decomposition stage facilitates the decomposition of jarosite.

#### Example 5

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A residue containing about 70% of Ag in jarosite was slurried with a 260 g/l NaCl solution at 70°C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to 145 kg Ca(OH)<sub>2</sub> per ton of sample, based on a stoichiometric excess of 20%, and the slurry was agitated for 2 hours. The slurry was then acidified to pH 2 by adding 131 kg H<sub>2</sub>SO<sub>4</sub> per ton of sample, and agitated for a further 5 hours.

To remove Fe from the circuit, limestone was added as a solid to establish a pH of 3.7. The solid residue was then separated from the brine solution. Overall Ag dissolution of 87% was obtained.

This illustrates the process of the invention when an iron removal stage is included.

#### Example 6

The same procedure was carried out as for example 2, except that the temperature during alkaline pretreatment was 50°C, not 70°C. Acid consumption in the acid leach step was 164 kg H<sub>2</sub>SO<sub>4</sub> per ton, and Ag dissolution was only 63%.

This example illustrates the importance of temperature in the alkaline treatment stage.

#### Example 7

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A residue containing about 70% of Ag in jarosite was slurried with a 260 g/l NaCl solution at (a) 70°C and (b) 80°C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to maintain a constant pH of 9 for both tests, and the slurry was agitated until no further lime additions were necessary to maintain the set pH. The slurries were then acidified to pH 2 by adding (a) 82 and (b) 87 kg H<sub>2</sub>SO<sub>4</sub> per ton of sample respectively, and agitated for a further 5 hours.

In both cases, Ag dissolution was 93%. However, where the alkali treatment was done at 70°C, 7.5 hours were required to complete this stage, while at 80°C, only 3 hours were required.

This example illustrates the effect of temperature and time on the proposed process.

#### **CLAIMS:**

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- A method to dissolve at least one metal from jarosite or other iron hydroxy sulfate containing-material which includes the steps of:
  - (c) subjecting the material to alkaline treatment in a brine solution to facilitate jarosite decomposition, and
  - (d) acidification of the brine slurry to solubilise the liberated metal.
- 2. A method according to claim 1 which includes the step of adjusting the pH of the brine slurry to remove solubilised iron or other impurities from the slurry followed by the step of separating metal-containing brine solution and solid residue from each other.
- 3. A method according to claim 2 which includes the step of removing metal value or values from the brine solution using a technique selected from: cementation, ion exchange, solvent extraction, electrowinning and precipitation.
- 4. A method according to claim 3 wherein, after the step of removing the metal value or values, barren brine liquor is recycled for use in the alkaline treatment (step (a)).
- 5. A method according to claim 4 which includes the steps of bleeding impurities from the barren brine liquor and adding NaCl and water to the barren brine liquor prior to the alkaline treatment.
- 6. A method according to any one of claims 1 to 5 wherein the temperature in the alkaline treatment stage is between 30°C and 100°C.

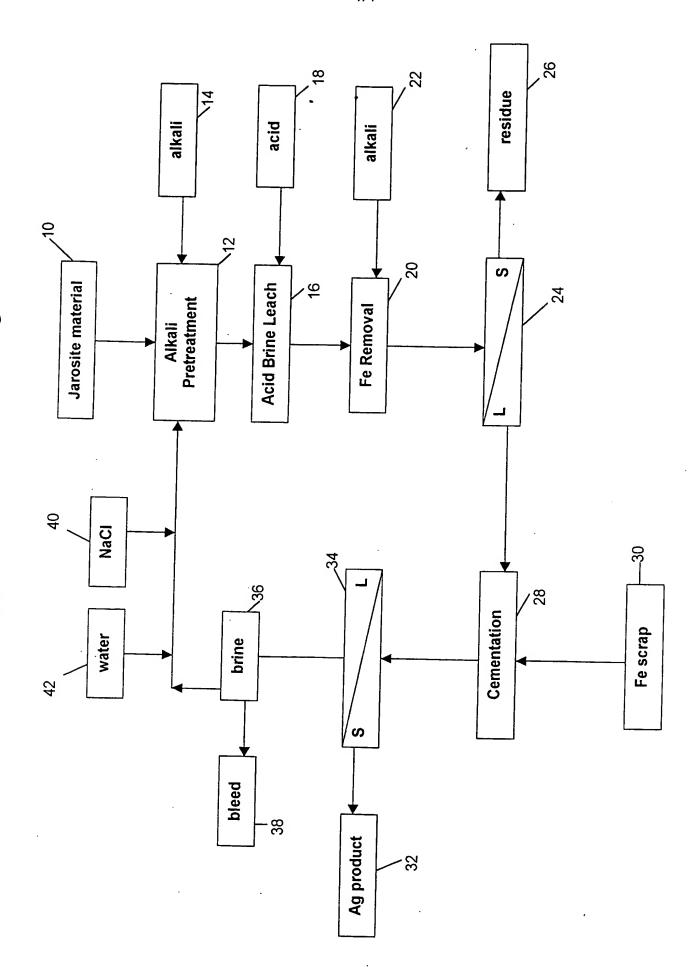
- 7. A method according to claim 6 wherein the temperature in the alkaline treatment stage is between 50°C to 90°C.
- 8. A method according to any one of claims 1 to 7 wherein the brine concentration of the brine solution is between 100g/l NaCl and saturation levels, or the equivalent of any other soluble chloride salt.
- A method according to claim 8 wherein the brine concentration of the brine solution is between 200g/I and 300g/I NaCI.
- 10. A method according to any one of claims 1 to 9 wherein the temperature of the brine slurry during step (b) is between 30°C and 100°C.
- 10 11. A method according to claim 10 wherein the temperature of the brine slurry during step (b) is between 50°C and 90°C.
  - 12. A method according to any one of claims 1 to 11 wherein the pH of the brine slurry during step (a) is above 7.
  - 13. A method according to claim 12 wherein the pH of the brine slurry during step (a) is between 9 and 13.
  - 14. A method according to any one of claims 1 to 13 wherein the pH of the brine slurry during step (b) is less than 6.
  - 15. A method according to claim 14 wherein the pH of the brine slurry during step (a) is between 1 and 3.

- 16. A method according to any one of claims 1 to 15 wherein the temperature of the slurry during step (b) is between 30°C and 100°C.
- 17. A method according to claim 16 wherein the temperature of the slurry during step (b) is between 70°C and 90°C.
- 5 18. A method according to any one of claims 1 to 17 wherein the duration of step (a) is less than 24 hours.
  - 19. A method according to any one of claims 1 to 18 wherein the duration of step (b) is less than 8 hours.
  - 20. A method according to any one of claims 1 to 19 wherein at least one metal is silver.

#### **REFERENCES**

- 1. Raghavan R, Mohanan PK, Swarnkar SR, 'Hydrometallurgical processing of lead-bearing materials for the recovery of lead and silver as lead concentrate and lead metal', Hydrometallurgy 58, 2000, p103-116.
- 5 2. Gallagher NP, Lei KPV, 'Recovery of lead and silver from plumbojarostie by hydrothermal sulfidation and chloride leaching', Report of Investigations 9277, US Department of the Interior, Bureau of Mines.
  - 3. Sandberg RG, Huiatt JL, 'Recovery of silver, gold, and lead from a complex sulfide ore using ferric chloride, thiourea, and brine leach solutions', Report of Investigations 9022, US Department of the Interior, Bureau of Mines.
  - 4. Bahr A, Proesemann T, 'Recovery of silver from refractory ores', XVI International Mineral Processing Congress, Stockholm, June 5-10, 1988, Part B. E Forssberg (Ed.).
- Martin D, Diaz G, 'Hydrometallurgical treatment of lead secondaries and/ore low grade concentrates: the Placid and Ledclor processes', Conference: Recycling lead and zinc the challenge of the 1990's, Rome 11-13 June 1991, International Lead and Zinc Study Group.
  - 6. Peters MA, Hazen WW, Reynolds JE, 'Process for recovering metal values from jarosite solids', US Patent 5078786, 7 January 1992.

- 7. Berezowsky RMGS, Stiksma J, Kerfoot DGE, Krysa BD, 'Silver and gold recovery from zinc pressure leach residue', Lead-Zinc '90, TS Mackey and RD Prengaman (Eds.), The Minerals, Metals and Materials Society, 1990.
- 8. Patino F, Salinas E, Cruells M, Roca A, 'Alkaline decomposition-cyanidation kinetics of argentian natrojarosite', Hydrometallurgy 49, 1998, p323-336.
- 9. Thompson P, Diaz M, Plenge G, 'Pressure oxidation of silver-bearing sulfide flotation concentrates', Mining Eng., September 1993, p1195-1200.



# **ABSTRACT**

A method to dissolve at least one metal from jarosite or other iron hydroxy sulfate containing-material which includes the steps of subjecting the material to alkaline treatment in a brine solution to facilitate jarosite decomposition, and acidification of the brine slurry to solubilise the liberated metal.

(Fig. 1)